



Construction double electric field of sulphur vacancies as medium ZnS/ Bi₂S₃-PVDF self-supported recoverable piezoelectric film photocatalyst for enhanced photocatalytic performance

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ABSTRACT

When internally polarized by mechanical energy, piezoelectric materials can establish polarization electric field and provide driving force for separating photogenerated carriers. Herein, S vacancies are introduced as an intermediate to make metal ions form coordination bond with F⁻ on PVDF (polyvinylidene fluoride) surface, and the built-in electric field is intimately related to polarized electric field. We successfully synthesized ZnS/Bi₂S₃-PVDF film photocatalyst containing S vacancies (ZnS-V_S/Bi₂S₃-PVDF). Polarized electric field on PVDF caused by ultrasonic cavitation and built-in electric field formed between ZnS-V_S/Bi₂S₃ heterojunction structure are beneficial to interfacial charge transferring. Theoretical calculation simulation demonstrate that the synergistic effect of the double electric fields is propitious to inhibit the recombination of carriers. The hydrogen evolution rate of ZnS-V_S/Bi₂S₃-PVDF reaches 10.07 mmol h⁻¹g⁻¹. Moreover, it has excellent reversibility and facile recovery capacity. This work provides new platform for photocatalytic reduction of hydrogen evolution and is expected to contribute to clean energy production.

1. Introduction

In recent years, with the rapid growth of population and the rapid development of social economy, the increasing demand for energy and the worsening environmental pollution have become two major problems [1–3]. Semiconductor photocatalysis technology has reveal great potential in environmental remediation and clean energy, hence it has attracted extensive attention and become one of the most popular academic issues in recent years [4–6].

Zinc sulfide (ZnS) is a promising semiconductor photocatalyst. it has high activity under ultraviolet light, but has no response under visible light [7,8]. At the same time, it is vulnerable to photocorrosion and electron cavitation composite, which limits its application in the field of photocatalysis [9,10]. Therefore, researchers carry out engineering strategies such as doping, coupling with semiconductors and introducing defect structures to solve the problem of easy recombination of electrons and holes in photocatalysts [11,12]. Jiang et al. constructed a strongly coupled heterojunction photocatalyst consisting of ZnS and Bi₂S₃. The interface of heterostructure makes carrier separation and transport effective [13]. Hao et al. constructed ZnS/g-C₃N₄

heterostructure, which cause the built-in electric field between ZnS and C₃N₄. So as to improve the photoinduced electron-hole separation capability [14]. Up to now, there are many reports about the heterojunction between ZnS nanoparticles and other semiconductors to form a built-in electric field, thus inhibiting the recombination of carriers. However, the interfacial electric field formed by the heterojunction structure has little intensity, narrow action range, weak driving force, and limited effect on the separation of photoelectric carriers. In order to solve the problem that the carrier is easy to recombination from the photocatalyst itself, introducing vacancies into photocatalyst can narrow the band gap to a certain extent, so as to achieve the purpose of expanding light absorption. At the same time, the introduction of vacancies makes it easier to capture photogenerated electrons, thus inhibiting the recombination of photogenerated electrons and holes. Nevertheless, introducing heterojunction structure and vacancy into photocatalysis has not fundamentally solved the problem of easy recombination of carriers, so it is urgent to find a reasonable way to effectively separate carriers.

Recently, constructing space electric field is an valid pattern to promote carrier separation [15]. However, it is rare to introduce the

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polarized electric field as driving force to effectively enhance the separation of carriers [16–18]. Piezoelectric materials capable of forming polarized electric fields have non-centrosymmetric structure [19]. The positive and negative charge centers of piezoelectric materials noncoincidence under the mechanical deformation or applied electric field, thus generating piezoelectric potential [20–22]. The piezoelectric potential can modulate the charge at the heterojunction and Schottky junction interface of photocatalyst to provide driving force for the separation carriers [23–25]. Typical piezoelectric materials include ZnO, CdS, MoS₂, BaTiO₃, etc [26–29]. But these inorganic piezoelectric materials are fragile, which greatly restrict their practical applications [30–32]. However, polymer piezoelectric materials have excellent flexibility, non-toxicity, high chemical stability and high piezoelectric coefficient, such as polyvinylidene fluoride (PVDF), polyvinyl fluoride (PVF), polyvinyl chloride (PVC) [33–35]. Yin et al. exploited PVDF to inhibit the recombination of photogenerated electrons and holes in MoS₂/g-C₃N₄ heterojunction photocatalyst to enhance photocatalytic performance [36]. Introducing piezoelectric effect into photocatalytic reaction is an effective way to inhibit recombination of carriers. However, simple recombination fails to fully connect the piezoelectric effect and the heterojunction structure to achieve the optimal synergistic effect.

In this work, we have designed hybrid ZnS-V_S/Bi₂S₃-PVDF recoverable self-supporting flexible film photocatalyst combined with PVDF and semiconductor materials. The introduction of S vacancies makes F[−] exposed by PVDF film occupy S vacancies and form Zn-F coordination bond. The S vacancies are used as a link to fully combine the built-in electric field with the polarized electric field. ZnS-V_S and Bi₂S₃ construct a heterojunction structure to form a built-in electric field, which effectively separates electrons and holes. Meanwhile, as flexible polymer piezoelectric material, PVDF is deformed under the action of ultrasonic waves, resulting in macroscopic polarization. Therefore, the polarized electric field formed at the interface between ZnS-V_S/Bi₂S₃ and PVDF is regarded as the driving force of carrier directional migration. The synergistic effect of double electric fields is conducive to improve carrier mobility and reduce recombination probability. This research work offers a new idea for the design of other high activity photocatalytic systems.

2. Experimental

2.1. Materials

Zinc chloride (ZnCl₂), bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), sodium sulfate (Na₂SO₄), sodium sulphide nonahydrate (Na₂S·9H₂O), sodium sulfite (Na₂SO₃), thiourea, polyvinylidene fluoride (PVDF) were bought from Aladdin Chemical Co., Ltd.

2.2. Hydrothermal synthesis of ZnS-V_S and ZnS

5 mmol ZnCl₂ and 5 mmol thiourea were added to 30 mL of ethanol solution. After about 30 min stirring, the clear solution was transferred to 50 mL Teflon-line stainless steel autoclave and heated at 160 °C for 12 h. The obtained precipitate was centrifuged, and washed with distilled water and ethanol for three times. Finally the trapped power was dried at 60 °C overnight. Pure ZnS was prepared by the same procedure mentioned above in the condition of changing thiourea to 9 mmol.

2.3. Hydrothermal synthesis of ZnS/Bi₂S₃ and ZnS-V_S/Bi₂S₃

The above 0.3 g ZnS-V_S, 0.032 mmol Bi(NO₃)₃·5H₂O and 0.56 mmol thiourea were added into 25 mL of ethanol, continuous stirring for 30 min. Then, the clear solution was transferred to 50 mL Teflon-line stainless steel autoclave and heated at 180 °C for 24 h. The obtained ZnS-V_S/Bi₂S₃ precipitate was centrifuged, and washed with distilled

water and ethanol for three times. Finally the trapped power was dried at 60 °C overnight. The synthesis of ZnS/Bi₂S₃ remains other conditions remain consistent, and ZnS-V_S nanoparticles are replaced by ZnS.

2.4. Preparation of ZnS-V_S/Bi₂S₃-PVDF film

0.5 g PVDF powder was completely dissolved in 5 mL DMF after continuous stirring for 2 h. Subsequently, the uniform transparent solution was formed. Then 0.5 g ZnS-V_S/Bi₂S₃ powder was added, and stir the solution vigorously for 1 h. After that, the obtained mixture was coated on glass slide with drop-coating. Finally, the coated product was cured in vacuum oven at 60 °C manufacture ZnS-V_S/Bi₂S₃-PVDF film.

2.5. Characterizations

The X-ray diffraction (XRD) on a Rigaku D/max-2000 diffractometer with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) was applied Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer by energy of 20 eV and Al Kα excitation source. Transmission electron microscope (TEM) and high resolution TEM (HRTEM) were performed on FEI Tecnai G2 S-Twin operating at 300 kV. The UV–vis spectrum of the product was received by spectrophotometer (HITACHI UH-4150). The photoluminescence (PL) spectrum was gained by HORIBA FluoroMax-4. In the presence of external pressure on the thin film photocatalyst, and named as ZnS-V_S/Bi₂S₃-PVDF-p (presence pressure). Pressure-free photocatalyst film was named ZnS-V_S/Bi₂S₃-PVDF-a (absence pressure).

2.6. Photocatalytic performance test

Generally, the above-mentioned ZnS-V_S/Bi₂S₃-PVDF film was placed in 45 mL of an aqueous solution containing 1.0 M Na₂S and 1.0 M Na₂SO₃ with continuous ultrasonic. The photocatalytic system was vacuumized three to clean remove the air before using the 300 W Xe lamp (PLS-SXE300D, Beijing Perfectlight). The temperature of the reaction vessel was maintained at 6 °C throughout the photocatalytic hydrogen evolution. The hydrogen content was monitored by gas chromatograph (Agilent 780A GC). The whole photocatalytic process was carried out under ultrasonic conditions. In order to prevent ultrasonic overheating, it is necessary to add ice bags into the ultrasonic machine and constantly change the water in the machine. The AQY is calculated as the formula: [13].

$$AQY = \frac{N_e}{N_p} \times \% = \frac{2 \times M \times N_A \times h \times c}{S \times P \times t \times \lambda} \quad (1)$$

where N_e is the number of electrons in the reaction, N_p is the incident photons, N_A is Avogadro constant, M is the number of molecules of H₂, c is the speed of light, h is the Planck constant, P is light intensity, S is the illumination area, t is the photoreaction time and λ is the wavelength of different incident light.

2.7. Photoelectrochemical test

The photoelectrochemical measurements were carried out on an electrochemical workstation with three-electrode system (CHI660C), Pt and Ag/AgCl as counter electrode and reference electrode. Xe lamp of 300 W ($\lambda \geq 420$ nm) was used as light source, meanwhile, the 0.5 M Na₂SO₃ aqueous solution was served as electrolyte.

3. Results and discussion

3.1. Morphology and structure characterization

The manufacturing route of ZnS-V_S/Bi₂S₃-PVDF film is shown in Fig. 1a. Firstly, ZnS-V_S/Bi₂S₃ nanoparticles are synthesized by typical

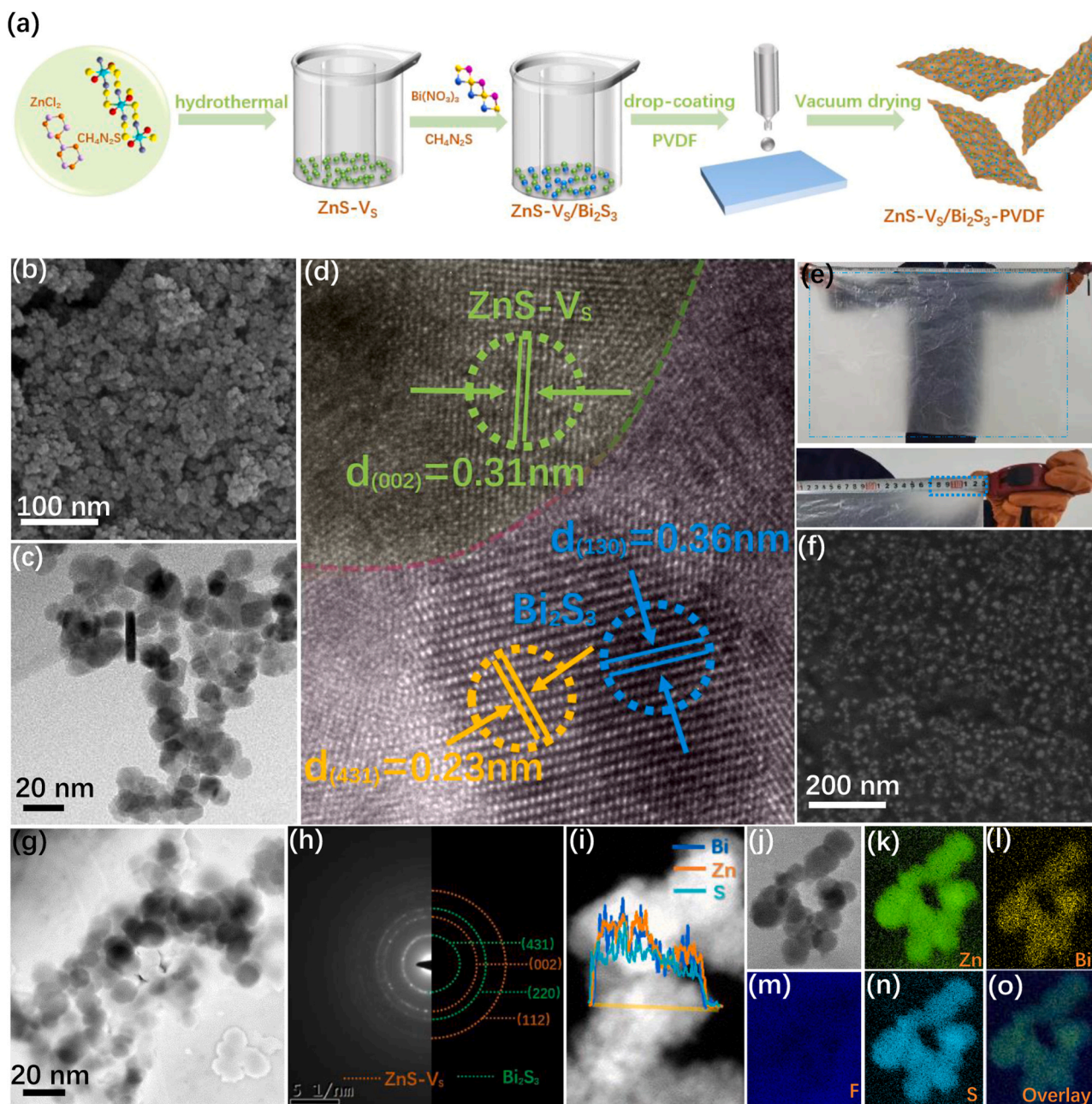


Fig. 1. (a) Schematic diagram of the fabrication process of ZnS-Vs/Bi₂S₃-PVDF. (b, c) SEM and TEM images of ZnS-Vs/Bi₂S₃ nanoparticles. (d) HRTEM image of ZnS-Vs/Bi₂S₃. (e) Photograph of ZnS-Vs/Bi₂S₃-PVDF film. (f, g) SEM and TEM images of ZnS-Vs/Bi₂S₃-PVDF. (h) SAED patterns of ZnS-Vs/Bi₂S₃. (i) Line scanning profile of ZnS-Vs/Bi₂S₃. (j-o) HAADF-STEM image of ZnS-Vs/Bi₂S₃-PVDF and elemental mapping of Zn, Bi, S, F and overlay.

hydrothermal method. Subsequently, the ZnS-Vs/Bi₂S₃-PVDF flexible film is prepared through spin coating process. The morphology and microstructure of ZnS-Vs/Bi₂S₃ are researched by SEM and TEM images. The morphology of the exposed ZnS-Vs/Bi₂S₃ is approximately regular microspheres with diameter of about 20 nm (Fig. 1b and c). HRTEM image further suggests that ZnS nanoparticles are closely connected to Bi₂S₃, forming compact interface between ZnS and Bi₂S₃ in the hybrid photocatalyst (Fig. 1d). Lattice fringe with lattice spacing of 0.31 nm can be labeled to (002) crystal planes of ZnS [37,38]. Meanwhile, the fringe spacing are 0.36 nm and 0.23 nm, which are exactly consistent with the (130) and (431) lattice plane of Bi₂S₃ [39]. As shown in Fig. S1a and S1b, the atoms in the yellow region are fuzzy and discontinuous, indicating that it is a region rich in S defects. The reason of S vacancies is that thiourea can not be completely translate into S²⁻ for chemical reaction. This will cause the problem of insufficient S source content, which

makes it impossible to form a face-centered cubic structure around Zn²⁺ in the form of four coordination. Therefore, S vacancies will appear in the crystal structure. The ZnS-Vs/Bi₂S₃-PVDF film with an area of 113 cm × 90 cm is prepared as illustrated in Fig. 1e. Its strong mechanical properties make it a promising photocatalyst. Simultaneously, it can be recovered from water without any time-consuming treatment. As shown in Fig. 1f and g, SEM and TEM images are applied to further observe the surface structure of ZnS-Vs/Bi₂S₃-PVDF film. ZnS and Bi₂S₃ nanoparticles are embedded in the flat PVDF film, and the size and morphology of nanoparticles are not affected by the film formation. The selected area electron diffraction (SAED) diagram shows a clear diffraction ring, indicating the high crystallinity of ZnS-Vs/Bi₂S₃. The diffraction ring in Fig. 1h demonstrate the existence of (002), (112) crystal planes of ZnS-Vs and (220), (431) crystal planes of Bi₂S₃. These diffraction rings are attributed to the polycrystalline property of the

ZnS-V_s/Bi₂S₃ nanoparticles. The linear scanning curve in Fig. 1i shows the existence of Zn, Bi and S elements in ZnS-V_s/Bi₂S₃ composite photocatalyst. Furthermore, the element mapping pattern clearly demonstrates that Zn, Bi, S and F exist in ZnS-V_s/Bi₂S₃-PVDF film photocatalyst, and F element is located in the whole region (Fig. 1j-o). The above results indicate that ZnS-V_s/Bi₂S₃-PVDF film photocatalyst has been successfully synthesized.

As shown in Fig. 2a, the pure PVDF film shows a X-ray characteristic diffraction peak at $2\theta = 18.4^\circ$, which indicates that PVDF film mainly forms β phase. Similar diffraction peaks can be observed from ZnS-V_s/Bi₂S₃-PVDF film. This shows that the addition of ZnS and Bi₂S₃ has little effect on the crystalline phase of PVDF film. It is obvious that the crystallinity of β phase in ZnS-V_s/Bi₂S₃-PVDF film is better than that of naked PVDF. This is mainly due to the Zn-F coordination bond between F⁻ exposed in PVDF and ZnS-V_s, which enhances the interface effect. It is more conducive to the formation of β phase [40]. All the peaks of samples are perfectly matched with ZnS (PDF#03-0524) and Bi₂S₃ (PDF#06-0333). Compared with ZnS/Bi₂S₃, the (002) diffraction peak position of ZnS-V_s/Bi₂S₃ gradually moves to a higher angle. The results show that the lattice in ZnS-V_s/Bi₂S₃ structure has changed. The interlayer stacking distance decreases slightly and the interlayer stacking density increases, which proves that there is a certain S vacancies. Moreover, it is concluded that ZnS nanoparticle is cubic and Bi₂S₃ nanoparticle is orthorhombic.

The surface chemical composition and state of the prepared samples are investigated by XPS. In Fig. 2b, the XPS spectrum of Zn 2p in ZnS/Bi₂S₃ has two peaks at 1021.6 eV and 1045.5 eV, which are classified as Zn 2p_{1/2} and Zn 2p_{3/2}. This indicates that the Zn element exists in the form of Zn²⁺ [41,42]. In addition, the binding energy of Zn 2p in ZnS-V_s/Bi₂S₃ photocatalyst gradually decreased. This result is attributed to S vacancies in the ZnS structure. The binding energies of Zn 2p_{1/2} and Zn 2p_{3/2} moved 1.52 eV towards the lower binding energies. We can reasonably infer that these peaks of Zn²⁺ are close to the S vacancies of single negative charge state. This leads to an increase in the electron density near the S vacancies and decrease in the binding energy of Zn²⁺. The binding energies of 158.2 eV and 163.9 eV are easily classified to Bi 4f_{7/2} and Bi 4f_{5/2} of Bi₂S₃. The S 2p of XPS spectra (Fig. 2c) appeared at

160.7 eV and 161.8 eV, completely consistent with the previously reported binding energies of S 2p_{3/2} and S 2p_{1/2} [43]. The above results show that the valence of Bi element in Bi₂S₃ nanocomposites is mainly +3, and the valence of S element is -2 [44].

It can be observed from Fig. 2c that the binding energy of Bi 4f of ZnS-V_s/Bi₂S₃ is higher than that of ZnS/Bi₂S₃, which is due to the difference of surface electron density. It has been reported that the change of binding energy is related to the difference of surface electron density. It is caused by electron transfer between semiconductors with different Fermi energy, electrons will transition from high energy level to low energy level [45]. Compared with the ZnS-V_s/Bi₂S₃ hybridization process, electrons are more inclined to transfer from Bi₂S₃ to ZnS-V_s. Therefore, the electron concentration in Bi₂S₃ decreases, and eventually the binding energy of Bi 4f is increased [46]. Meanwhile, the peak area of S in ZnS-V_s/Bi₂S₃ is lower than that in ZnS/Bi₂S₃, which further indicates the existence of S vacancies in the ZnS structure. The XPS peak at 685.3 eV is attributed to the existence of Zn-F coordination bond (Fig. 2d). The illustration clearly shows the structure diagram of Zn-F coordination bond formed by F⁻ on PVDF surface occupying S vacancy in ZnS. Furthermore, the valence band (VB) of the sample is determined by the XPS spectrum in Fig. S3. The VB of ZnS and ZnS-V_s are 2.84 eV (relative to the Fermi level), the VB of Bi₂S₃ is 0.94 eV.

Fourier transform infrared spectroscopy (FTIR) is used to analyze the structure of PVDF and ZnS-V_s/Bi₂S₃-PVDF. Fig. 2e reveals the FTIR of PVDF and ZnS-V_s/Bi₂S₃-PVDF films. The absorption bands at 602 cm⁻¹, 680 cm⁻¹, 868 cm⁻¹ and 1403 cm⁻¹ represent the β crystalline phase in PVDF [47]. The absorption band at 836 cm⁻¹ corresponds to the C—C bond rocking vibration in PVDF [48]. Meanwhile, the absorption peak near 1166 cm⁻¹ is attributed to the tensile vibration of C—H [49]. Compared with ZnS-V_s/Bi₂S₃-PVDF films, the absorption peak frequency and band shape of PVDF are basically the same, which manifest that the functional groups of PVDF have not changed substantially. However, the intensity of some absorption peaks has changed. The absorption peaks at 1065 cm⁻¹ is considered to be the tensile vibration of C—F. The strength of ZnS-V_s/Bi₂S₃-PVDF film is weakened, indicating that the interaction between F atoms and C atoms is weakened [50]. The trend of absorption peak intensity indicates that Zn²⁺ can form

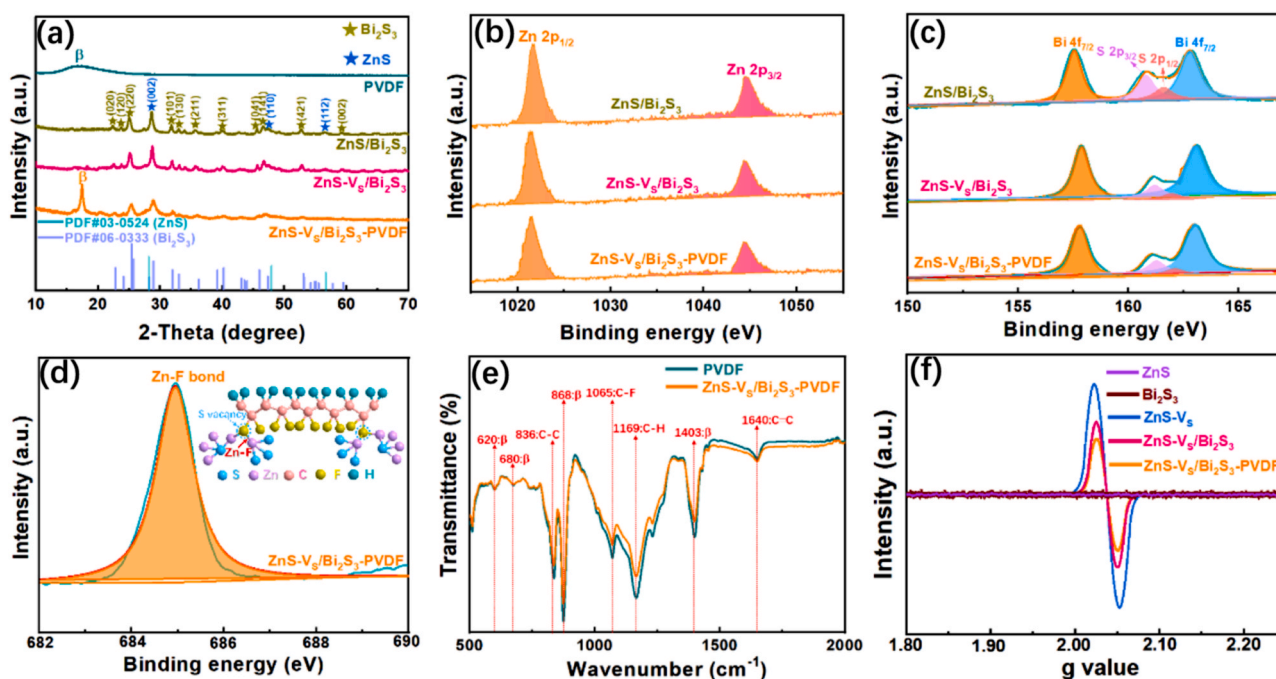


Fig. 2. (a) XRD pattern of PVDF, ZnS-V_s, ZnS/Bi₂S₃, ZnS-V_s/Bi₂S₃ and ZnS-V_s/Bi₂S₃-PVDF. XPS spectra of ZnS/Bi₂S₃, ZnS-V_s/Bi₂S₃ and ZnS-V_s/Bi₂S₃-PVDF nanocomposite: (b) Zn 2p, (c) Bi 4f and S 2p. (d) F 1s of ZnS-V_s/Bi₂S₃-PVDF (The illustration is a schematic diagram of Zn-F coordination bond formed by PVDF and ZnS-V_s). (e) FTIR spectra of PVDF film and ZnS-V_s/Bi₂S₃-PVDF films. (f) EPR spectra of ZnS, ZnS-V_s, Bi₂S₃, ZnS-V_s/Bi₂S₃ and ZnS-V_s/Bi₂S₃-PVDF.

coordination covalent bond with F⁻. Due to the induction of Zn²⁺, the vibration coupling of C—F bond is weakened. Therefore, the absorption peaks of C—F are reduced, while the absorption peaks of C=C and C—H are enhanced [51]. The change of absorption peak at 1640 cm⁻¹ corresponds to the absorption peak of C=C. The formation of Zn—F bond leads to partial defluorination of PVDF, the content of C=C in ZnS-V_S/Bi₂S₃-PVDF film increases to some extent [48]. Above all, it is proved that Zn-F coordination bond exists in ZnS-V_S/Bi₂S₃-PVDF.

Fig. 2f shows the EPR spectra of different samples. $g = 2.003$ is the electronic paramagnetic resonance signal. There is no obvious characteristic peak in ZnS at $g = 2.003$, but there is an obvious characteristic peak in ZnS-V_S, which indicates that ZnS with S vacancies has been successfully synthesized [52]. ZnS-V_S/Bi₂S₃ also has characteristic peaks, however its intensity is lower than ZnS-V_S. This indicates that some S vacancies are filled in the process of compounding Bi₂S₃. The EPR signal of ZnS-V_S/Bi₂S₃-PVDF is lower than that of ZnS-V_S/Bi₂S₃. The possible reason is that the exposed F⁻ in PVDF film occupies the position of S vacancies and forms Zn-F coordination bond, which makes the S vacancies occupied by filling to some extent.

3.2. Piezoelectric characterization

Piezoresponse force microscopy (PFM) is a significant measure to characterize the microcosmic domain structure of ferroelectric materials [53]. The strength of piezoelectric response can be expressed by the vibration amplitude and phase at the same position of the membrane. A sharp contrast can be observed in the piezoelectric response amplitude diagram (Fig. 3a). The phase image in Fig. 3b has 180° domains, which indicates that ZnS-V_S/Bi₂S₃-PVDF film shows excellent piezoelectricity in a certain polarization direction. Moreover, in order to further verify

the piezoelectric performance, the piezoelectric hysteresis curve and butterfly curve are measured in Fig. 3c and d. The apparent butterfly curve and distinct square phase curve indicate that ZnS-V_S/Bi₂S₃-PVDF film has piezoelectric characteristics and polarization response conversion behaviors. When the applied voltage is reversed from +10 V to -10 V, the phase reversal of ZnS-V_S/Bi₂S₃-PVDF film approaches 180°. The results show that ZnS-V_S/Bi₂S₃-PVDF film has favorable piezoelectric properties.

3.3. Photochemical and electrochemical characterization

The optical properties of ZnS, ZnS/Bi₂S₃, ZnS-V_S/Bi₂S₃, ZnS-V_S/Bi₂S₃-PVDF are probed through UV-vis diffuse reflectance spectra. As shown in Fig. 4a, compared with pure ZnS, the absorption edge of the ZnS/Bi₂S₃ composite appear red shift from 510 nm to 615 nm. The consequence reveal that the ZnS/Bi₂S₃ heterojunction composite can make victorious utilize of sunlight, thus it is expected to improve the photocatalytic performance. At the same time, compared with ZnS/Bi₂S₃ photocatalyst, ZnS-V_S/Bi₂S₃ sample exhibit more apparent visible light absorption intensity and expanded absorption edge. The results explain that the existence of S vacancies is conducive to enhance light absorption ability. There is no significant transform between the absorption edges of ZnS-V_S/Bi₂S₃ and ZnS-V_S/Bi₂S₃-PVDF, indicating that PVDF has insubstantial appliance for enhancing the absorption of visible light. Simultaneously, the band structure of the ZnS, ZnS-V_S and Bi₂S₃ corresponding to the visible region (Fig. S2 and S4) are calculated by the altered Kubelka-Munk function ($ah\nu = A(h\nu - E_g)$), in which $h\nu$ is the photon energy, E_g is the band gap, A is the constant). The E_g values of ZnS, ZnS-V_S and Bi₂S₃ are 3.47 eV, 3.38 eV and 1.77 eV.

The surface photovoltage (SPV) signal in Fig. 4b determines the

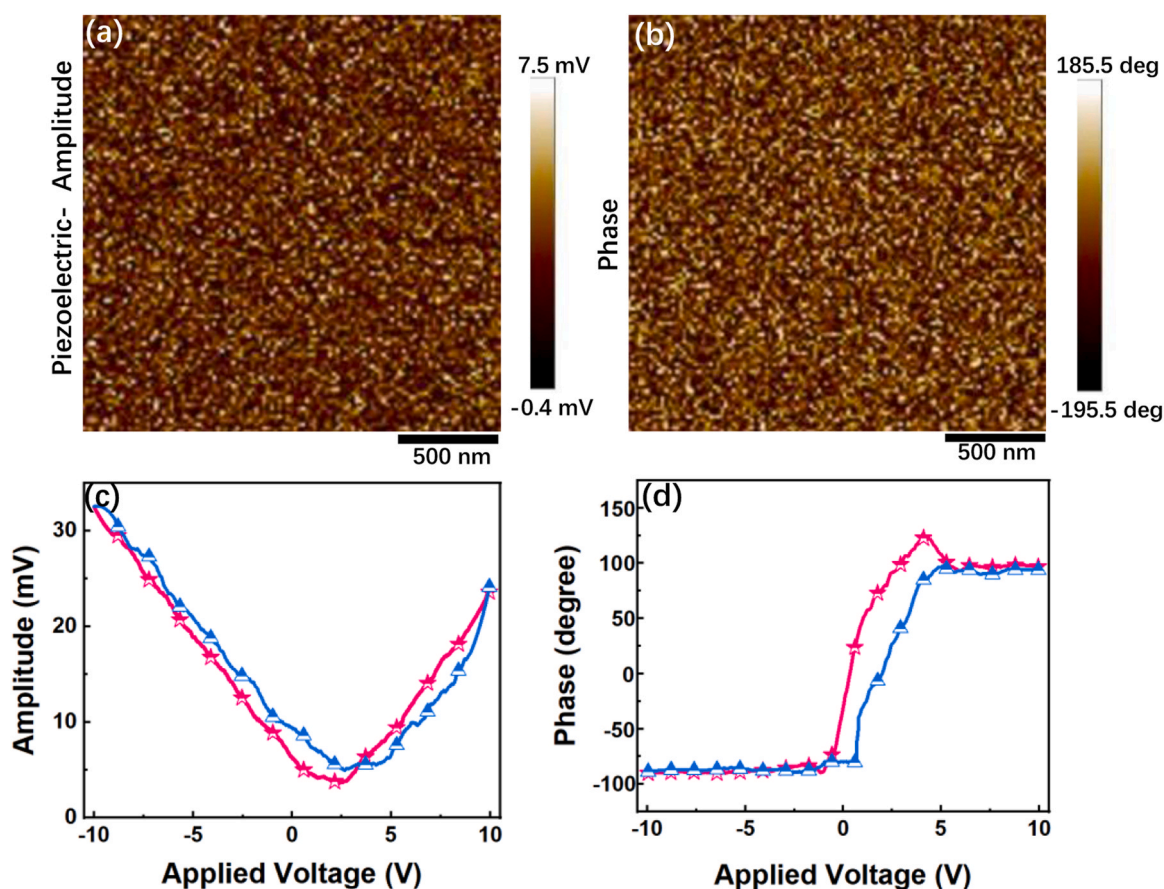


Fig. 3. (a) PFM piezoelectric amplitude and (b) phase images of ZnS-V_S/Bi₂S₃-PVDF film. (c) butterfly loops and (d) piezoelectric hysteresis of ZnS-V_S/Bi₂S₃-PVDF film.

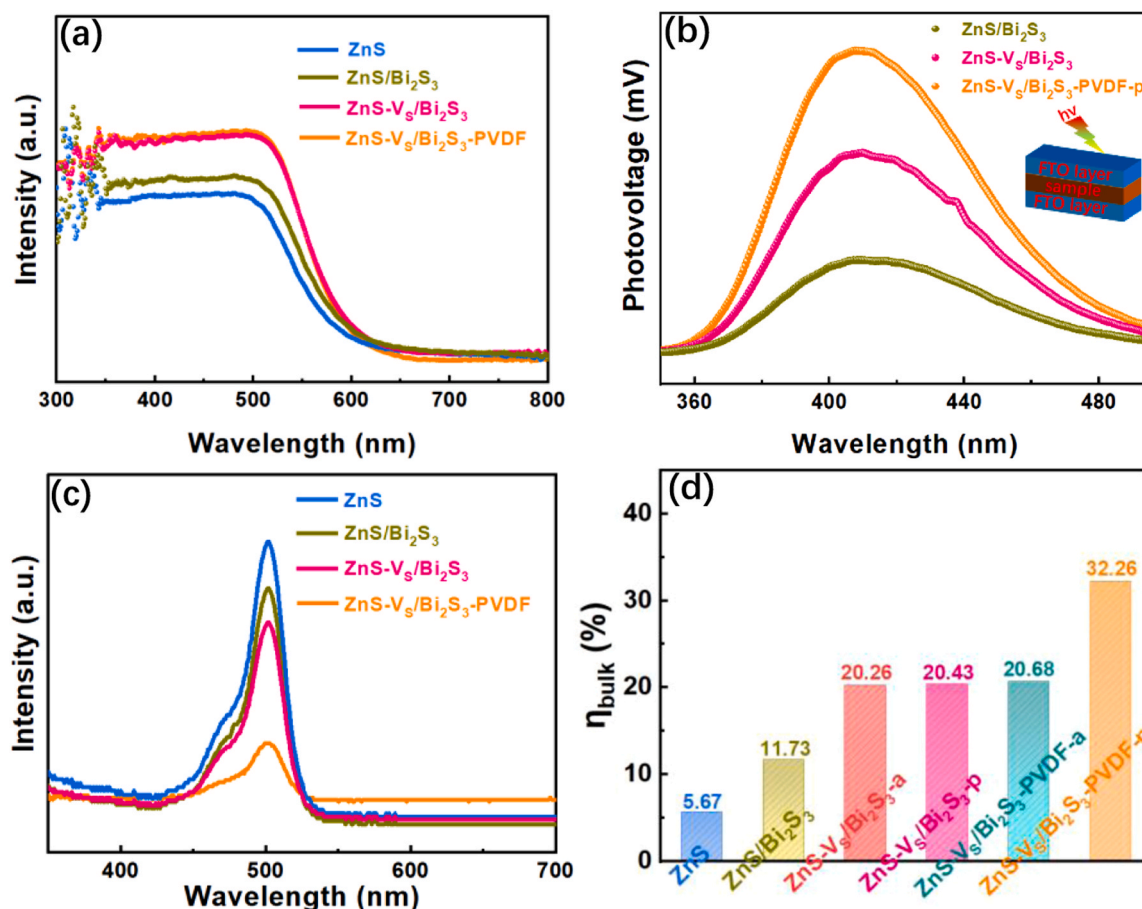


Fig. 4. (a) UV-vis diffuse reflection spectrum of ZnS, ZnS/Bi₂S₃, ZnS-V_s/Bi₂S₃ and ZnS-V_s/Bi₂S₃-PVDF. (b) Surface photovoltage (c) The PL spectra of ZnS, ZnS/Bi₂S₃, ZnS-V_s/Bi₂S₃, ZnS-V_s/Bi₂S₃-PVDF. (d) bulk-charge separation efficiency (η_{bulk}) of different photocatalysts.

carrier migration behavior [55]. The SPV signal of ZnS-V_s/Bi₂S₃-PVDF-p is higher than that of other samples, which can be attributed to two reasons. One reason is ZnS-V_s/Bi₂S₃ constructs heterojunction structure to form an internal electric field. It can accelerate the separation of light-induced carriers and the migration of electrons on the interface of heterogeneous structures. The other reason is the polarization electric field constructed by the piezoelectric effect of PVDF to enhance the separation of carriers. The synergistic effect of double electric fields reduces the recombination probability of carriers in ZnS-V_s/Bi₂S₃-PVDF-p thin film photocatalyst. As plotted in Fig. 4c, ZnS photocatalyst display strong PL peak, which illustrated that more carriers are formed and reassembled rapidly. The internal electric field formed between heterojunctions can effectively promote the carrier separation, which makes the PL intensity of ZnS/Bi₂S₃ decrease obviously. The PL intensity of ZnS-V_s/Bi₂S₃ is further reduced, which revealed that the existence of S vacancy can significantly improve the lifetime of carriers. The PL strength of ZnS-V_s/Bi₂S₃-PVDF films is significantly reduced after deformation. This is due to the piezoelectric polarization electric field induced by the macroscopic polarization of PVDF film to some extent.

The Zeta potential is applied to characterize the amount of charge on the surface of particles. The Zeta potential of ZnS-V_s/Bi₂S₃-PVDF-p is -37.45 mV, while the ZnS, ZnS/Bi₂S₃, ZnS-V_s/Bi₂S₃-a, ZnS-V_s/Bi₂S₃-p and ZnS-V_s/Bi₂S₃-PVDF-a are -10.83 mV, -18.16 mV, -27.69 mV, -27.83 mV and -28.41 mV, respectively (Fig. S5). Compared with ZnS-V_s/Bi₂S₃-p, the Zeta potential of ZnS-V_s/Bi₂S₃-PVDF-a is almost the same, which further proves that the change of ZnS-V_s/Bi₂S₃-PVDF-p Zeta potential is caused by the piezoelectric effect produced by PVDF rather than ultrasound effect. The Zeta potential of ZnS-V_s/Bi₂S₃-PVDF-

a has changed compared with ZnS-V_s/Bi₂S₃-a. The reason for the potential reduction of ZnS-V_s/Bi₂S₃ is that nanoparticles are partially embedded in PVDF film. The PVDF film itself also has a certain charge, these two factors together leads to tiny improvement in the potential of ZnS-V_s/Bi₂S₃-PVDF-a. ZnS-V_s/Bi₂S₃-PVDF-p has the highest Zeta potential, illustration that it has the strongest electric field. It is conducive to improving the separation and transmission of charge.

Quantitative measurements of bulk-charge separation efficiency (η_{bulk}) for different photocatalysts are made using the formula reported by Kim and colleagues [54]. The η_{bulk} of ZnS, ZnS/Bi₂S₃, ZnS-V_s/Bi₂S₃-a, ZnS-V_s/Bi₂S₃-p, ZnS-V_s/Bi₂S₃-PVDF-a and ZnS-V_s/Bi₂S₃-PVDF-p are estimated to be $\approx 5.67\%$, $\approx 11.73\%$, $\approx 20.26\%$, $\approx 20.43\%$, $\approx 20.68\%$ and $\approx 32.26\%$, respectively. This high η_{bulk} indicates that the carrier separation is more distinct, so that more electrons have the opportunity to participate in the photocatalytic hydrogen evolution reaction (Fig. 4d).

The linear scanning voltammetry (LSV) curves in Fig. 5a illustrate the charge transfer kinetics of the sample. S vacancy in ZnS-V_s/Bi₂S₃ can capture photogenerated electrons, which makes the hydrogen evolution potential of ZnS-V_s/Bi₂S₃ composite is lower than that of ZnS/Bi₂S₃. Thereby improving the charge density and carrier separation efficiency. External pressure is applied to ZnS-V_s/Bi₂S₃-PVDF thin films to randomly orient the dipoles in PVDF. Thus, the charge transfer at the interface between semiconductor and PVDF thin films is facilitated, and the hydrogen evolution potential is reduced. Simultaneously, the Tafel slope of ZnS-V_s/Bi₂S₃-PVDF-p ($195 \text{ mV} \cdot \text{dec}^{-1}$) is smaller than that of ZnS-V_s/Bi₂S₃ ($227 \text{ mV} \cdot \text{dec}^{-1}$) and ZnS/Bi₂S₃ ($283 \text{ mV} \cdot \text{dec}^{-1}$). The above results reveal that ZnS-V_s/Bi₂S₃-PVDF-p has excellent efficiency in the photocatalytic hydrogen evolution reaction.

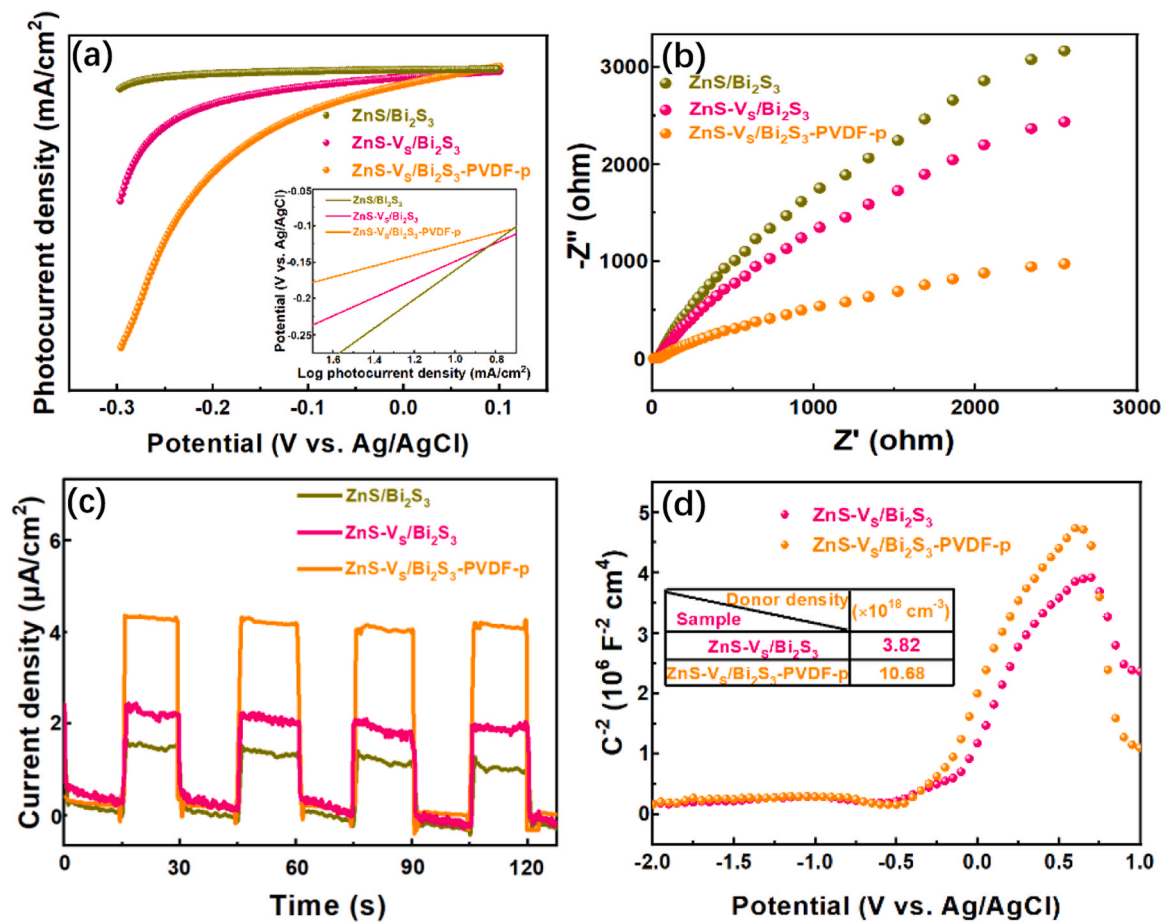


Fig. 5. (a) LSV curves (The insert is Tafel slopes). (b) EIS Nyquist plots, (c) transient photocurrent responses of ZnS/Bi₂S₃, ZnS-V_s/Bi₂S₃ and ZnS-V_s/Bi₂S₃-PVDF-p. (d) Mott-Schottky curves of ZnS-V_s/Bi₂S₃ and ZnS-V_s/Bi₂S₃-PVDF-p. The insert in Fig. 5d is parameter calculated by Mott-Schottky plots.

The EIS Nyquist diagram in Fig. 5b shows that the semi-circular arc represents the charge transfer process. The smaller arc radius of ZnS-V_s/Bi₂S₃-PVDF-p proves that charge carriers can move smoothly with less impulse. In addition, the transient photocurrent response under the irradiation of excited light is shown in Fig. 5c. It can be seen that the photocurrent increases rapidly with the switching on of light, indicating the generation of photogenerated electrons and holes. As the light is taken away, the photocurrent rapidly drops down zero due to the quick recombination of electron-hole pairs. The transient photocurrent of ZnS-V_s/Bi₂S₃-PVDF-p photocatalyst is much higher than that of other samples. These results once again prove that well-designed photocatalyst is helpful for charge separation. When the piezoelectric electric field is applied, the carriers in the piezoelectric copolymer will drift [56]. Positive piezoelectric charges attract electrons in semiconductor and negative electric charges attract holes in semiconductor. Thereby effectively separating electrons and holes in the semiconductor [57].

The pivotal parameters in the Mott-Schottky curve are devoted to calculate the carriers concentration of the photocatalyst, according to formula: [58].

$$N_D = - \left\{ \frac{2}{e\epsilon\epsilon_0} \right\} \left\{ \frac{d(1/C^2)}{dE} \right\}^{-1} \quad (2)$$

e is the unit charge, ϵ_0 is the vacuum permittivity, ϵ is the relative permittivity, C is the space charges capacitance of the semiconductor, N_D is the carriers concentration, E is the electrode potential, respectively. Fig. 5d demonstrates the change of carriers concentration of ZnS-V_s/Bi₂S₃ and ZnS-V_s/Bi₂S₃-PVDF-p under piezoelectric potential. When external pressure is applied to ZnS-V_s/Bi₂S₃, the electron concentration

increases from $3.83 \times 10^{18} \text{ cm}^{-3}$ to $10.68 \times 10^{18} \text{ cm}^{-3}$. This will result in the accumulation of local positive piezoelectric charges. Thus, the electron-hole pairs produced by light are separated by a piezoelectric potential. So more electrons can participate in the photocatalytic hydrogen production reaction.

3.4. Photocatalytic hydrogen evolution activity

The photocatalytic activity is evaluated by hydrogen production rate of different samples under visible light. The schematic diagram of the photocatalytic reaction device and the reaction process are shown in Fig. S6 and Video S1. Fig. 6a reveals the hydrogen evolution rate by ZnS, ZnS-V_s, ZnS/Bi₂S₃, ZnS-V_s/Bi₂S₃, ZnS-V_s/Bi₂S₃-PVDF-a and ZnS-V_s/Bi₂S₃-PVDF-p within 2.5 h. The hydrogen evolution rate of ZnS-V_s ($1.57 \text{ mmol h}^{-1} \text{ g}^{-1}$) is 1.69 times that of ZnS nanoparticles ($0.93 \text{ mmol h}^{-1} \text{ g}^{-1}$). This is due to the existence of S vacancy enhances the utilization rate of visible light and as the active site of the reaction, so that its photocatalytic activity is improved. The hydrogen evolution rate of ZnS/Bi₂S₃ ($1.77 \text{ mmol h}^{-1} \text{ g}^{-1}$) is 1.90 times that of ZnS nanoparticles ($0.93 \text{ mmol h}^{-1} \text{ g}^{-1}$). The reason is that the heterojunction interface between ZnS and Bi₂S₃ is conducive to the separation of charge carriers. Meanwhile, the hydrogen generation rate of ZnS-V_s/Bi₂S₃ ($4.84 \text{ mmol h}^{-1} \text{ g}^{-1}$) is 2.73 times that of ZnS/Bi₂S₃ ($1.77 \text{ mmol h}^{-1} \text{ g}^{-1}$). The hydrogen production rate of ZnS-V_s/Bi₂S₃-PVDF-a has almost no obvious change compared with that of ZnS-V_s/Bi₂S₃. In the absence of pressure, PVDF has no contribution to the separation and transfer of carriers. Under ultrasonic excitation, the rate of hydrogen production of ZnS-V_s/Bi₂S₃-PVDF-p can reach $10.07 \text{ mmol h}^{-1} \text{ g}^{-1}$. The external mechanical force causes PVDF to generate polarized electric field, which

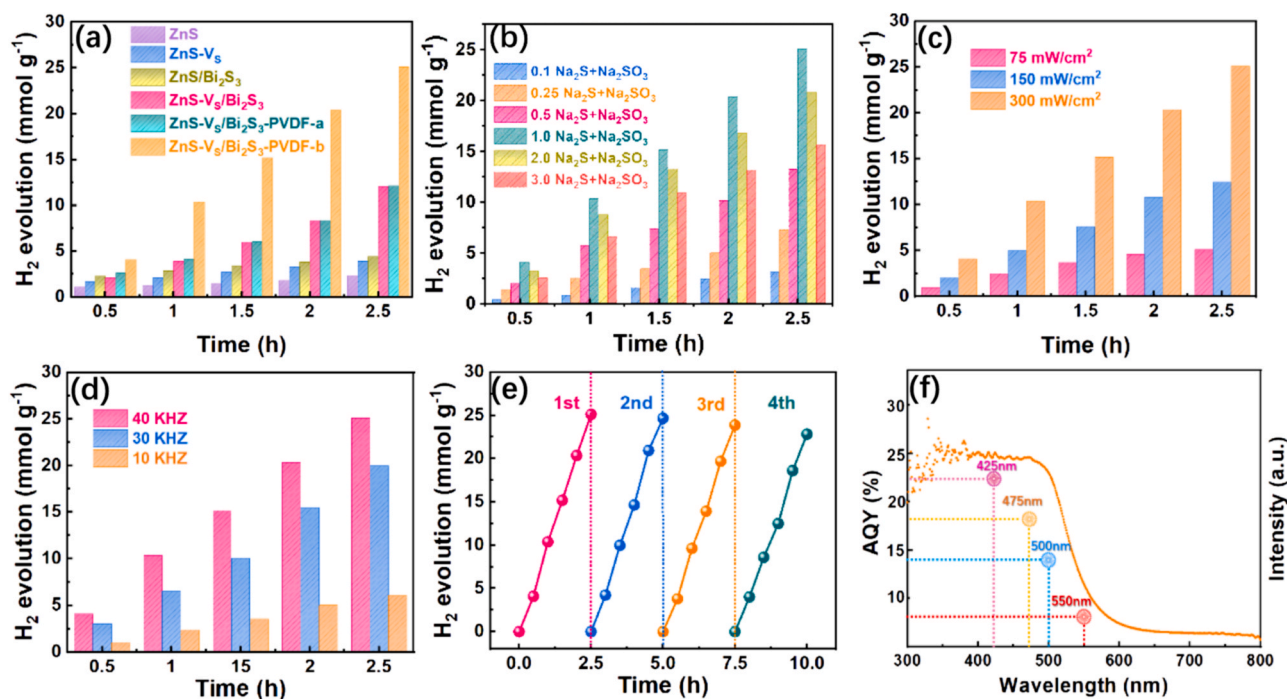


Fig. 6. Hydrogen evolution rate of (a) different photocatalysts, (b) different concentrations of sacrificial agent, (c) different optical power density, (d) different ultrasonic intensity. (e) Cyclic stability of ZnS-Vs/Bi₂S₃-PVDF-p under Xe lamp. (f) The apparent quantum yield of ZnS-Vs/Bi₂S₃-PVDF-p under different monochromatic light illumination.

effectively controls the carrier migration direction and separation efficiency.

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In order to investigate the influence of external mechanical pressure on the photocatalyst performance, the pressure is applied by stirring (Fig. S7). It is found that the hydrogen production rate of ZnS-Vs/Bi₂S₃-PVDF-p is also obviously affected, which shows that the piezoelectric effect of PVDF under ultrasound is the most prominent. At the same time, the influence of different rotational speeds on hydrogen production rate is examined. The greater the rotational speed, the greater the pressure exerted on PVDF, resulting in the stronger piezoelectric effect. The hydrogen production rate is 4.43 mmol h⁻¹g⁻¹ at 200 rpm and 6.19 mmol h⁻¹g⁻¹ at 800 rpm. Table S1 shows the hydrogen production activity of metal sulfide photocatalysts in recent literature, and our work has excellent photocatalytic hydrogen production rate. Table S2 compares the hydrogen production efficiency of ZnS-Vs/Bi₂S₃-PVDF-p with other piezoelectric photocatalysts. The results show that the synergistic effect of polarized electric field and built-in electric field are conducive to carrier separation and improve photocatalytic activity.

The hydrogen evolution rate is positively correlated with the sacrificial agent concentration. The sacrificial agent can trap the holes and make the electrons and holes separated effectively [59]. As shown in Fig. 6b, when the concentration of the sacrificial agent is 1.0 M (Na₂S+Na₂SO₃), the hydrogen production efficiency of ZnS-Vs/Bi₂S₃-PVDF-p reaches the maximum value of 10.07 mmol h⁻¹g⁻¹. With the increase of sacrificial agent concentration, the hydrogen evolution of ZnS-Vs/Bi₂S₃-PVDF-p decreased. The reason for this phenomenon is that S will be produced during the photocatalytic reaction, and S will cover the appearance of ZnS-Vs/Bi₂S₃-PVDF photocatalyst. For one thing, the S coating prevents the incidence of light and reduces the utilization rate of visible light. For another thing, the S layer covers the active sites on the photocatalyst surface, which reduces the photocatalytic hydrogen production efficiency. Fig. 6c shows the correlation between Xe lamp power density and hydrogen generation rate. The higher the power density of the laser,

the more likely it is to excite the electrons participating in the photocatalytic reaction. The Xe lamp power density is 150 mW/cm², the hydrogen production rate reaches 4.99 mmol h⁻¹g⁻¹. The hydrogen production rate is 2.03 mmol h⁻¹g⁻¹ at 75 mW/cm².

The change of mechanical force will promote the separation of electrons and holes in different degrees. Fig. 6d demonstrate the effect of vibration power on hydrogen production rate. The hydrogen production of mechanical vibration at 10 kHz frequency (2.42 mmol h⁻¹g⁻¹) is much lower than that at 40 kHz vibration power. The performance of ZnS-Vs/Bi₂S₃-PVDF-p can be stable and reusable under continuous illumination for more than 10 h as shown in Fig. 6e. The film after photocatalytic reaction can be directly recovered from the reaction solution. This indicates that ZnS-Vs/Bi₂S₃-PVDF-p has excellent reversibility and effortless recovery (Fig. S8). Moreover, the SEM images of ZnS-Vs/Bi₂S₃ and ZnS-Vs/Bi₂S₃-PVDF after photocatalytic reaction (Fig. S9). Their morphology and size have almost unchanged, which manifest that the ZnS-Vs/Bi₂S₃ and ZnS-Vs/Bi₂S₃-PVDF photocatalyst have high stability. In order to further verify the stability of ZnS-Vs/Bi₂S₃-PVDF, the reaction system of ZnS-Vs/Bi₂S₃-PVDF is detected by inductively coupled plasma (ICP) method. After four cycles, the concentrations of Zn²⁺ and Bi³⁺ can be neglected (Fig. S10). In addition, the F⁻ concentration is detected by ion chromatography, and the F⁻ concentration hardly changed before and after photocatalytic reaction (Table S3). The above results indicate that ZnS-Vs/Bi₂S₃-PVDF membrane can exist stably. In order to confirm the uniformity of ZnS-Vs/Bi₂S₃-PVDF film, six parts with equal area are cut out on the large area film for photocatalytic hydrogen evolution test. As shown in Fig. S11, the photocatalytic hydrogen evolution efficiency of the six parts are almost equal, which indicates the uniformity of ZnS-Vs/Bi₂S₃-PVDF membrane.

The apparent quantum yield (AQY) associated with the wavelength of ZnS-Vs/Bi₂S₃-PVDF-p exposed to different monochromatic light is shown in Fig. 6f. The AQY of ZnS-Vs/Bi₂S₃-PVDF-p can reach 23.6% at the wavelength of 425 nm. This is similar to the trend of UV-vis spectrum. Meanwhile, as shown in Fig. S12, the AQY of ZnS-Vs/Bi₂S₃-PVDF-p (25.8%) under visible light irradiation is 2.18 times that of ZnS/Bi₂S₃

(11.8%). Table S4 shows the AQY of metal sulfide photocatalysts in recent literature, and our work has excellent AQY. This is attributed to the synergistic effect of polarized electric field and built-in electric field by ZnS-V_S/Bi₂S₃-PVDF film. Thereby promoting the charge separation, accelerating the carrier migration rate and prolonging the carrier life.

3.5. Simulation theoretical calculation

So as to probe the correlation between pressure action and piezoelectric potential, we utilized COMSOL Multiphysics 5.4 to simulate calculation. Fig. 7 explores the change of PVDF piezoelectric potential under different pressures. The simulated dimension of the PVDF film is $20 \times 150 \times 1 \text{ nm}^3$. The polar axis of the simulated PVDF membrane is oriented along the z axis. Other parameters used in simulation, such as elastic matrix, coupling matrix, and relative permittivity of PVDF can be used as predetermined parameters in COMSOL Multiphysics 5.4. The consequence received from this is that the piezoelectric potential in the PVDF film is continuously distributed along the polar axis. When PVDF is subjected to ultrasonic wave, positive and negative potential will be generated on the opposite side. In addition, the potential value increases continuously, because the larger the proportion of polarization plane. The resulting piezoelectric potential and piezoelectric current are greater. The piezoelectric potential of PVDF under 10^3 Pa pressure is 180 mV. When the bubble with cavitation effect caused by ultrasonic wave breaks, the impact force on the catalyst can reach up to 10^8 Pa and the maximum piezoelectric potential is 1.38 V. Therefore, in the process of piezoelectric photocatalysis, the piezoelectric polarization electric field caused by ultrasonic activation promotes the orderly migration of carriers. This leads to a high photoelectric conversion process of the ZnS-V_S/Bi₂S₃-PVDF compound.

In order to further explore the effect of S vacancy, theoretical model are established under the framework of density functional theory (DFT). Their electronic properties are studied by first principles calculations. The band gap can be obtained from the electronic structure of Fig. 8a, c and e. Obviously, the band gap of ZnS with S vacancies is smaller than that of ZnS, which is consistent with the results of UV-vis diffuse reflection spectrum. In addition, ZnS with S vacancies exhibits different electronic structures from ZnS. This is due to the contribution of atomic orbitals, indicating that the introduction of S vacancies has a great influence on the electronic properties. At the same time, the more electrons are accumulated in the region where the band structure curve is concentrated. Fig. 8b shows that CB of ZnS-V_S is mainly composed of Zn 3p and S 3p, while VB consists of Zn 4s and S 3s. The presence of S vacancies in the ZnS crystal structure is more conducive to the transition of electrons from the VB to the CB under radiation, thereby increasing the carrier concentration. The electric field in the space charge region

will increase more conducive to promoting charge separation. Fig. 8d shows that CB of ZnS is composed of Zn 4s, Zn 3d and S 3s orbitals, and VB is Zn 3d and S 3p orbitals. The VB electrons in ZnS are easily excited due to the low degree of hybridization between Zn atoms and adjacent S atoms in VB. However, due to the high density of the hybrid electron cloud near the Zn atoms and S atoms in CB. Therefore, most of the CB electrons are transferred in ZnS, which causes a high degree of recombination of photogenerated carriers. As for Bi₂S₃, CB is mainly composed of Bi 6p and S 3s; VB consists of Bi 6p and S 3p orbitals (Fig. 8f). The mixed electron density of Bi atoms and adjacent S atoms is high, which will enhance the electrostatic attraction between the nucleus and electrons. In the ZnS-V_S and Bi₂S₃ heterojunction structure, the CB electrons in ZnS-V_S and the VB of Bi₂S₃ holes are more active. This may play a decisive role in the charge transfer kinetics in the ZnS-V_S/Bi₂S₃ composite. The above results reveal the energy band structure and orbitals of ZnS, ZnS-V_S and Bi₂S₃. This is beneficial to grasp the way of charge migration.

The density functional theory (DFT) are calculated to investigate the charge transfer approach in the heterojunction of ZnS-V_S and Bi₂S₃. As shown in Fig. 8g and h, ZnS-V_S has low surface work function and weak binding ability to electrons. Hence, it can effectively accelerate photo-generated charge migration and promote surface reaction. As described in Fig. 8h and i, the work function of Bi₂S₃ (4.52 eV) is smaller than that of ZnS-V_S (5.27 eV). When the two Fermi levels (E_f) are different, the interface electron transfer process will occur between Bi₂S₃ and ZnS-V_S. Eventually their E_f are aligned with the same height. Since semiconductor E_f is a factor that directly affects the density of clustered electrons, it can be expressed by the following formula: [60,61].

$$E_f = E_{CB} + KT \ln \frac{n_c}{N_c} \quad (3)$$

where E_{CB} represents the CB energy, n_c is the cumulative electron density and N_c is the carrier density of the semiconductor. Specifically, accumulated electrons will be transferred from Bi₂S₃ to ZnS-V_S by means of heterojunctions. This charge flow causes a built-in electric field to be formed near the interface, which can effectively control the migration and separation of photogenerated.

3.6. Photocatalytic mechanism

PVDF is an excellent polymer piezoelectric film. When it is deformed by external force, the polarization phenomenon will be generated inside. This will cause positive and negative charges present to the two relative surfaces. The spontaneous polarization of PVDF can be generated by mechanical ultrasound. It can effectively convert the external force into electric energy and generate polarization electric field. ZnS-V_S and Bi₂S₃

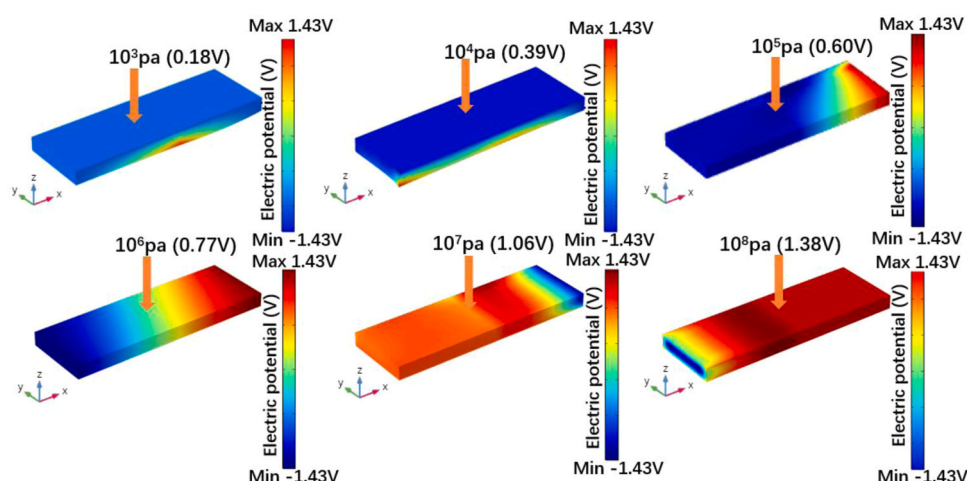


Fig. 7. COMSOL simulates the potential distribution of piezoelectric PVDF films under different pressures.

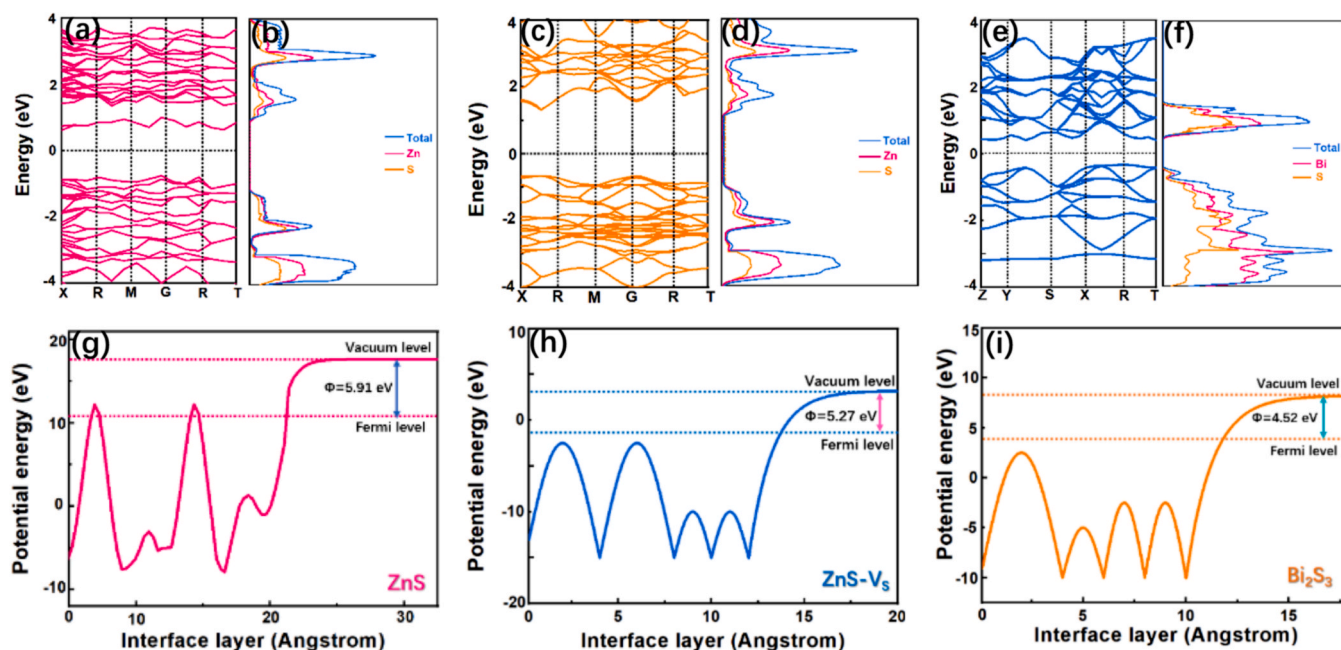


Fig. 8. Energy band structures of (a) ZnS-Vs (c) ZnS and (e) Bi₂S₃. Density of states of (b) ZnS-Vs (d) ZnS and (f) Bi₂S₃. (g, h, i) DFT calculated potential diagrams of ZnS, ZnS-Vs and Bi₂S₃ surfaces in vacuum.

are in close contact to form a heterojunction structure. Due to the difference of their Fermi level and carrier concentration, carrier diffusion occurs between ZnS-Vs and Bi₂S₃. Meanwhile, space charge regions are formed on both sides of the interface between ZnS-Vs and Bi₂S₃. Because the interface state is not considered, the charges in space form an internal electric field. The existence of built-in electric field can effectively enhance the separation efficiency of carriers and inhibit charge recombination (Fig. 9a). Introduce S vacancies promotes F⁻ on PVDF surface to occupy vacancies in ZnS to form Zn-F coordinate bond, which closely links polarized electric field with built-in electric field (Fig. 9b). The synergistic effect of this double electric field greatly improves the separation of carriers in the semiconductor, and then effectively improves the photocatalytic hydrogen evolution activity.

4. Conclusion

In summary, recoverable ZnS/Bi₂S₃-PVDF self-supporting photocatalyst film containing S vacancies are constructed. The synergistic

effect of the built-in electric field generated by ZnS-Vs/Bi₂S₃ heterojunction structure and the polarized electric field generated by PVDF are used to accelerate the separation of carriers, thus enhance the photocatalytic hydrogen evolution activity. The introduction of S vacancies makes F⁻ ions exposed on PVDF surface form Zn-F bond with Zn ions, which makes the built-in electric field closely integrated with polarized electric field. Meanwhile, the effects of internal electric field and polarized electric field are investigated through DFT calculation and COMSOL simulation. The hydrogen evolution rate of ZnS-Vs/Bi₂S₃-PVDF reaches 10.07 mmol h⁻¹g⁻¹. Photocatalyst self-supported films still maintain excellent stability after multiple cycles. Its structure has no obvious damage and is facile to recover after photocatalytic reaction. These work provides an innovative way for the construction of efficient photocatalytic system.

CRediT authorship contribution statement

Meng Li: Writing – original draft, Conceptualization, Methodology,

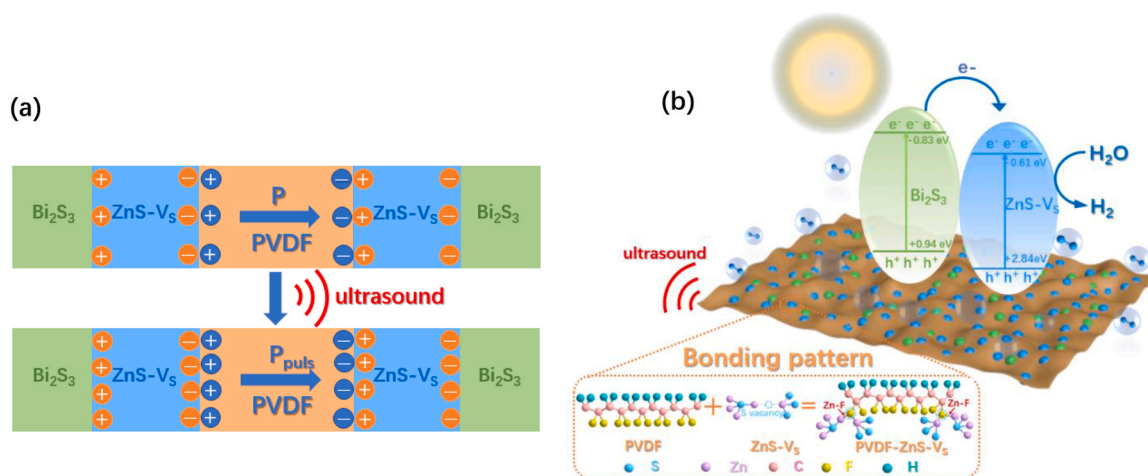


Fig. 9. (a) Polarization schematic diagram of PVDF under ultrasonic conditions. (b) Schematic diagram of the photocatalytic mechanism of ZnS-Vs/Bi₂S₃-PVDF under visible light irradiation.

Visualization, Investigation. **Jingxue Sun**: Supervision, Validation, Writing – review & editing, Funding acquisition. **Gang Chen**: Supervision, Validation, Methodology. **Shunyu Yao**: Investigation. **Bowen Cong**: Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2021.120792.

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